Supplementary Materials: Characteristics and Potential Inhalation Exposure Risks of Environmentally Persistent Free Radicals in Atmospheric Particulate Matter and Solid Fuel Combustion Particles in High Lung Cancer Incidence Area, China

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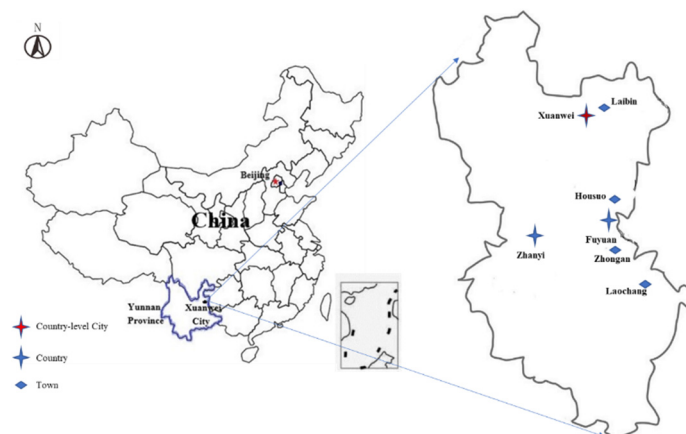
Figure S1. Sampling sites [28].

In this study, we collected a total of 3 types of samples: three kinds of raw biomass (Pine, Corncob, Poplar) from Zhongan Town, six kinds of residential raw coal from Bole Town (Luomu coal (LM) and Bole coal (BL)), Houshou Town (Lijiawu coal (LJW)), Laochang Town (Shunfa coal (SF)), Laibin Town (Guangming coal (GM) and Zongfan coal (ZF)), and eight group of APMs (Houshou Town) were collected.
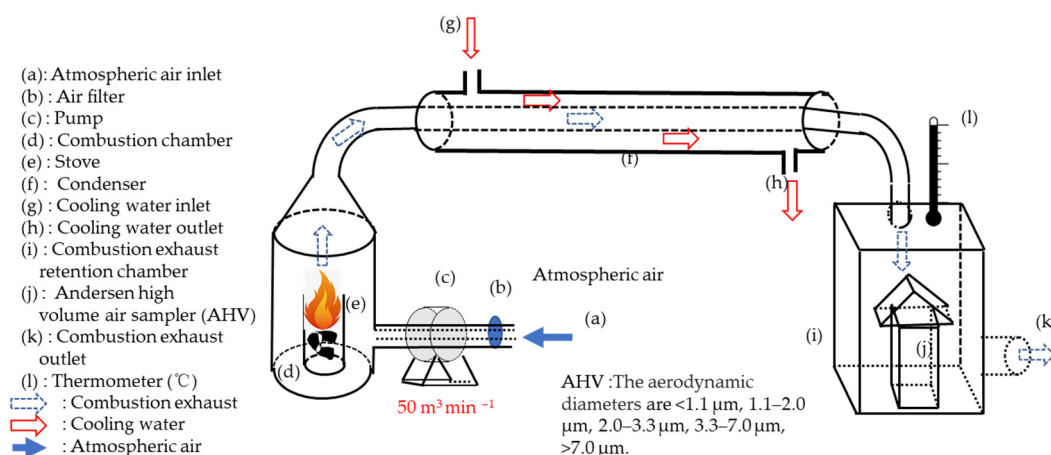

(a): Atmospheric air inlet
(b) : Air filter
(c) : Pump
(d) : Combustion chamber
(e) : Stove
(f) : Condenser
(g) : Cooling water inlet
(h) : Cooling water outlet
(i) : Combustion exhaust retention chamber
(j) : Andersen high volume air sampler (AHV)
(k) : Combustion exhaust outlet
(l) : Thermometer (℃)
- - - : Combustion exhaust
⇨ : Cooling water
➤ : Atmospheric air

Atmospheric air

50 m³ min⁻¹

AHV :The aerodynamic diameters are <1.1 µm, 1.1–2.0 µm, 2.0–3.3 µm, 3.3–7.0 µm, >7.0 µm.

Figure S2. Sketch of sampling system [28].

The details information on simulated combustion systems and processes was presented in the Figure S2 from my previous study[28].The flue gas collection system consists of a flue device and sampler. The flue device consists of a closed trumpet-shaped hood, two elbows and a cooling water sleeve. In addition, a closed flue gas holding chamber is connected to the end of the flue, and Andersen high volume air sampler (Shibata Science Co., Ltd., Japan) is placed in it. Several parts of the sampling system can be disassembled for easy cleaning, and they are connected by flanges. In order to avoid the pollution of the flue material to the flue gas, the entire flue device is made of stainless steel. The gasket used in the connection part is Teflon material.

Before simulating combustion, all parts of the sampling system are carefully cleaned. Move the solid fuel block ignited with alcohol to the furnace and place the coal furnace directly under the horn hood. The closed horn-shaped hood introduces clean air through the blower. In order to minimize the background pollution during sampling, it is convenient for experimental analysis. The flue gas is fully mixed by the flue device through the function of the sampler's pump and blower, and the temperature is reduced at the cooling water jacket. Finally, the flue gas temperature at the sampler is controlled at about 40 ℃. During the experiment, ensure that there is no flue gas leakage during the entire coal combustion process, and there is no obvious particle deposition in the pipeline.

Pre-treatment of filters has been consistent in our previous studies [9]. Before and after each sampling, the filters were weighed by sing an electronic balance with a detection limit of 0.01 mg (Sartorius, Co., Ltd., Germany). The Andersen sampler is placed horizontally in the flue gas holding chamber. The particles in five sizes were collected, with a flow rate at 566 L/min, and the aerodynamic diameter are <1.1 μm, 1.1–2.0 μm, 2.0–3.3 μm, 3.3–7.0 μm, and >7.0 μm, respectively.
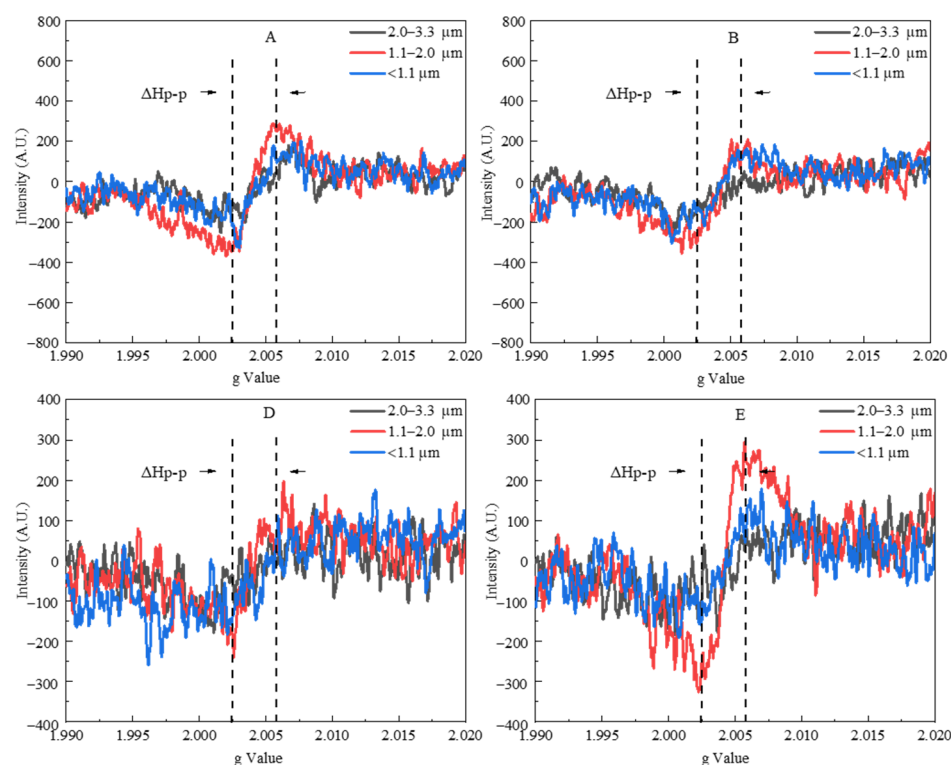
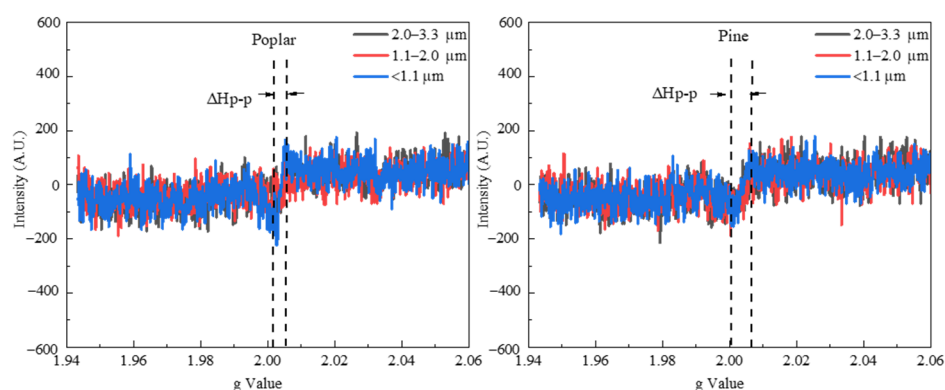**Figure S3.** The EPR spectra of EPFRs in APMs particulate matters.

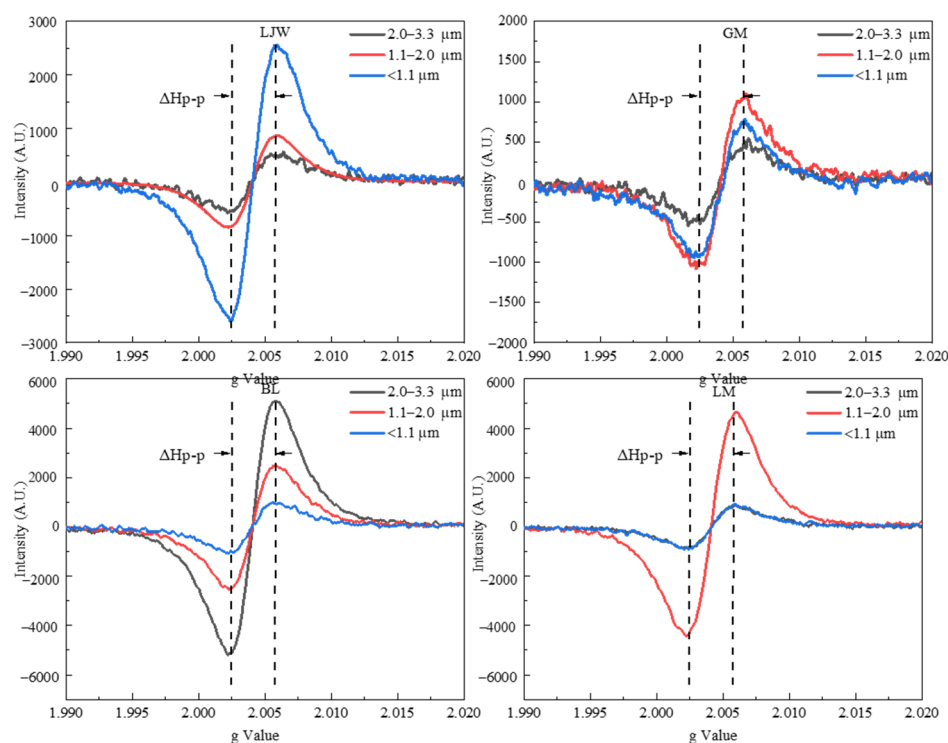**Figure S4.** The EPR spectra of EPFRs in biomass burning particulate matters.

Figure S5. The EPR spectra of EPFRs in coal burning particulate matters.

Table S1. Records of atmospheric particulate matter collected in Yunnan residential areas in 2017.

Num.	Start	End	Duration h	Volume L/min	Weather	Temperature	AQI	PM2.5	PM10
A	2017.2.18 AM9：40	2017.2.20AM9:40	48	566	2.18 Sunny	9–17℃	67	42	66
					2.19 Sunny	9–22℃	85	29	50
					2.20 Cloudy-Sunny	9–21℃	44	26	44
B	2017.2.20AM10:20	2017.2.22AM11:20	48	566	2.20 Cloudy-Sunny	9–21℃	44	26	44
					2.21Cloudy-Sunny	8–20℃	59	33	68
					2.22 Cloudy	9–20℃	62	25	73
C	2017.2.22AM11:30	2017.2.24AM11：30	48	566	2.22 Cloudy	9–20℃	62	25	73
					2.23 Light rain	8–19℃	40	26	35
					2.24 Light rain	3–6℃	38	26	38
D	2017.2.24AM11:50	2017.2.25AM11:50	48	566	2.24 Light rain	3–6℃	38	26	38
					2.25 Light rain	−1–2℃	50	30	50
E		2017.2.27PM1:40	48	566	2.25 Light rain	−1–2℃	50	30	50

					2.26 Light rain	0–2℃	72	52	81
F	2017.2.25PM1:40 2017.2.27PM2:20	2017.3.1PM2:20	43	566	2.27 Light rain	3–8℃	58	38	63
					2.28 Light rain	3–14℃	73	53	84
					3.1 Light rain	1–8℃	49	34	47
G	2017.3.2PM1:10	2017.3.3PM1:15	24	566	3.2 Light rain to cloudy	3–14℃	127	64	204
					3.3Sunny–Cloudy	8–19℃	82	60	101
H	2017.3.3PM5：30	2017.3.4PM5:30	24	566	3.3 Sunny–Cloudy	8–19℃	82	60	101
					3.4 Cloudy	8–19℃	78	45	105

Table S2. EPFRs and PM concentrations in biomass combustion particles.

Samples	1.1 µm			1.1–2.0 µm			2.0–3.3 µm		
	Spins/m³	Spins/g	µg/m³	Spins/m³	Spins/g	µg/m³	Spins/m³	Spins/g	µg/m³
Corncob	4.51×10^{17}	3.11×10^{15}	1781.82	1.04×10^{17}	1.30×10^{15}	985.86	6.19×10^{16}	9.28×10^{14}	820.20
Pine	4.27×10^{17}	3.37×10^{15}	2088.89	4.22×10^{16}	8.29×10^{14}	840.40	5.09×10^{16}	1.29×10^{15}	648.48
Poplar	3.26×10^{17}	1.08×10^{15}	4975.61	7.13×10^{16}	4.86×10^{14}	2420.05	4.59×10^{16}	4.22×10^{14}	1794.04
Average	4.01×10^{17}	2.52×10^{15}	2948.77	7.25×10^{16}	8.72×10^{14}	1415.44	5.29×10^{16}	8.80×10^{14}	1087.57
Min	3.26×10^{17}	1.08×10^{15}	1781.82	4.22×10^{16}	4.86×10^{14}	840.40	4.59×10^{16}	4.22×10^{14}	648.48
Max	4.51×10^{17}	3.37×10^{15}	4975.61	1.04×10^{17}	1.30×10^{15}	2420.05	6.19×10^{16}	1.29×10^{15}	1794.04
STD	5.42×10^{16}	1.02×10^{15}	1438.66	2.52×10^{16}	3.34×10^{14}	712.85	6.68×10^{15}	3.56×10^{14}	504.44

Min: Minimum value, Max: Maximum value, STD: Standard Deviation

Table S3. EPFRs and PM concentrations in coal combustion particles.

Samples	1.1 µm			1.1–2.0 µm			2.0–3.3 µm		
	Spins/m³	Spins/g	µg/m³	Spins/m³	Spins/g	µg/m³	Spins/m³	Spins/g	µg/m³
BL	2.10×10^{17}	6.51×10^{15}	2193.76	5.06×10^{16}	2.36×10^{15}	1457.60	1.01×10^{17}	3.73×10^{15}	1833.04
LM	1.87×10^{17}	2.93×10^{15}	4340.40	8.26×10^{16}	1.60×10^{15}	3514.43	2.40×10^{16}	1.10×10^{15}	1487.04
SF	2.25×10^{17}	2.32×10^{15}	6606.30	1.95×10^{16}	3.58×10^{14}	3697.00	3.07×10^{16}	1.46×10^{15}	1432.57
LJW	3.36×10^{17}	3.64×10^{15}	6277.97	1.51×10^{16}	1.84×10^{14}	5555.06	2.29×10^{16}	6.22×10^{14}	2497.06
GM	1.88×10^{17}	1.27×10^{16}	1008.54	2.57×10^{16}	2.18×10^{15}	802.41	2.48×10^{16}	2.92×10^{15}	577.15
ZF	1.51×10^{17}	4.25×10^{15}	2410.19	2.88×10^{16}	1.10×10^{15}	1775.62	1.69×10^{16}	1.91×10^{15}	600.71
Average	2.16×10^{16}	5.39×10^{15}	3806.19	3.70×10^{16}	1.30×10^{15}	2800.35	3.67×10^{16}	1.96×10^{15}	1404.60
Min	1.51×10^{17}	2.32×10^{15}	1008.54	1.51×10^{16}	1.84×10^{14}	802.41	1.69×10^{16}	6.22×10^{14}	577.15
Max	3.36×10^{17}	1.27×10^{16}	6606.30	8.26×10^{16}	2.36×10^{15}	5555.06	1.10×10^{17}	3.73×10^{15}	2497.06
STD	5.82×10^{17}	3.52×10^{15}	2105.99	2.33×10^{16}	8.31×10^{14}	1620.04	2.89×10^{16}	1.07×10^{15}	672.75

Min: Minimum value, Max: Maximum value, STD: Standard Deviation

Table S4. EPFRs and PM concentrations in atmospheric particulate matters.

Samples	1.1 µm			1.1–2.0 µm			2.0–3.3 µm		
	Spins/m³	Spins/g	µg/m³	Spins/m³	Spins/g	µg/m³	Spins/m³	Spins/g	µg/m³
A	8.50×10^{15}	2.23×10^{17}	62.08	1.24×10^{15}	8.72×10^{16}	23.25	1.34×10^{15}	1.10×10^{17}	19.94
B	6.61×10^{15}	1.55×10^{17}	69.69	8.71×10^{14}	5.90×10^{16}	24.06	7.08×10^{14}	4.88×10^{16}	23.62
C	3.14×10^{15}	1.63×10^{17}	31.41	4.95×10^{14}	5.16×10^{16}	20.8	4.95×10^{14}	5.16×10^{16}	15.64
D	1.79×10^{16}	4.26×10^{17}	34.23	1.16×10^{14}	4.17×10^{16}	22.82	1.16×10^{15}	4.17×10^{16}	22.58
E	2.86×10^{15}	1.44×10^{17}	32.39	7.39×10^{14}	3.21×10^{16}	37.48	6.99×10^{14}	5.19×10^{16}	21.96
F	3.17×10^{15}	1.86×10^{17}	27.73	9.24×10^{14}	5.09×10^{16}	29.57	6.07×10^{14}	5.27×10^{16}	18.77
Average	7.03×10^{15}	2.16×10^{17}	42.92	9.05×10^{14}	5.38×10^{16}	26.33	8.35×10^{14}	5.95×10^{16}	20.42

Min	2.86×10^{15}	1.44×10^{17}	27.73	4.95×10^{14}	3.21×10^{16}	20.80	4.95×10^{14}	4.17×10^{16}	15.64
Max	1.79×10^{16}	4.26×10^{17}	69.69	1.24×10^{15}	8.72×10^{16}	37.48	1.34×10^{15}	1.10×10^{17}	23.62
STD	5.29×10^{15}	9.73×10^{16}	16.50	2.50×10^{14}	1.72×10^{16}	5.66	3.06×10^{14}	2.29×10^{16}	2.68

Min: Minimum value, Max: Maximum value, STD: Standard Deviation

Table S5. g–values and ΔH_{P-P} of the EPFRs produced by different PM from Xuanwei.

Sample type	Sample groups	<1.1 μm		1.1–2.0 μm		2.0–3.3 μm	
		g–factors	ΔHp–p (Gauss)	g-factors	ΔHp–p (Gauss)	g-factors	ΔHp–p (Gauss)
Coal	BL	2.0041	5.6404	2.0039	5.6647	2.0039	5.8357
	LM	2.0041	5.5670	2.0039	5.4205	2.0039	5.5670
	SF	2.0041	6.2996	2.0039	6.5193	2.0040	5.9333
	LJW	2.0038	5.4694	2.0039	5.9089	2.0039	5.9333
	GM	2.0041	6.5193	2.0043	6.2996	2.0041	6.5682
	ZF	2.0041	5.6648	2.0016	5.5182	2.0041	5.2741
	Average	2.0040	5.8601	2.0036	5.8885	2.0040	5.8519
	STD	0.0001	0.3985	0.0009	0.4028	0.0001	0.3962
Biomass	Poplar	2.0042	3.8335	2.0043	2.2219	2.0042	6.1043
	Pine	2.0039	8.4239	2.0040	4.8590	2.0039	8.6680
	Corncob	2.0039	6.0554	2.0041	4.2730	2.0039	6.0798
	Average	2.0040	6.1043	2.0041	3.7846	2.0040	6.9507
	STD	0.0001	1.8743	0.0001	1.1306	0.0001	1.2144
APMs	A	2.0046	6.8612	2.0048	4.6148	2.0046	9.0098
	B	2.0044	8.1064	2.0041	6.0554	2.0044	9.3517
	C	2.0039	4.8834	2.0043	5.3474	2.0041	1.7581
	D	2.0039	16.0420	2.0039	6.7635	2.0039	9.3029
	E	2.0042	11.0853	2.0042	6.1042	2.0044	9.4738
	F	2.0042	5.5915	2.0044	4.9811	2.0042	3.4672
	Average	2.0042	8.7616	2.0043	5.6444	2.0043	7.0606
	STD	0.0002	3.8196	0.0003	0.7327	0.0002	3.1867

STD: Standard Deviation

Table S6. The potential health risk of EPFRs for adults and child per year.

Sample type	Sample groups	<1.1 μm		1.1–2.0 μm		2.0−3.3 μm		3.3 μm	
		EQ(Adult)	EQ(child)	EQ(Adult)	EQ(child)	EQ(Adult)	EQ(child)	EQ(Adult)	EQ(child)
Coal	BL	126.57	48.10	30.48	11.58	60.62	23.04	217.68	82.72
	LM	112.90	42.90	49.75	18.91	14.48	5.50	177.13	67.31
	SF	135.69	51.56	135.69	51.56	18.51	7.03	165.94	63.06
	LJW	202.37	76.90	9.07	3.45	13.78	5.24	225.21	85.58
	GM	113.39	43.09	15.47	5.88	14.94	5.68	143.80	54.64
	ZF	90.91	34.55	17.35	6.59	10.18	3.87	118.44	45.01
	Average	130.31	49.52	42.97	16.33	22.09	8.39	174.70	66.39
	Min	90.91	34.55	9.07	3.45	10.18	3.87	118.44	45.01
	Max	202.37	76.90	135.69	51.56	60.62	23.04	225.21	85.58
	STD	35.06	13.32	43.51	16.54	17.40	6.61	37.86	14.39
Biomass	Poplar	49.15	18.68	11.37	4.32	6.75	2.57	67.27	25.56

	Pine	62.48	23.74	6.18	2.35	7.44	2.83	76.10	28.92
	Corncob	47.71	18.13	10.44	3.97	6.71	2.55	64.86	24.65
	Average	53.11	20.18	9.33	3.54	6.97	2.65	69.41	26.37
	Min	47.71	18.13	6.18	2.35	6.71	2.55	64.86	24.65
	Max	62.48	23.74	11.37	4.32	7.44	2.83	76.10	28.92
	STD	6.65	2.53	2.26	0.86	0.34	0.13	4.83	1.84
APMs	A	122.91	46.70	17.97	6.83	19.44	7.39	160.31	60.92
	B	95.56	36.31	95.56	36.31	10.23	3.89	118.38	44.98
	C	45.34	17.23	45.34	17.23	7.16	2.72	64.52	24.52
	D	129.24	49.11	6.51	2.47	8.35	3.17	144.11	54.76
	E	41.33	15.70	10.68	4.06	10.10	3.84	62.11	23.60
	F	45.76	17.39	13.35	5.07	13.35	5.07	67.88	25.79
	Average	80.02	30.41	31.57	12.00	11.44	4.35	102.88	39.10
	Min	41.33	15.70	6.51	2.47	7.16	2.72	62.11	23.60
	Max	129.24	49.11	95.56	36.31	19.44	7.39	160.31	60.92
	STD	37.37	14.20	31.27	11.88	4.06	1.54	39.99	15.20

Min: Minimum value, Max: Maximum value, STD: Standard Deviation

[9]   Xiao, K.; Qin, A.; Wang, W.; Lu, S.; Wang, Q. Study on the Characteristics of Size-Segregated Particulate Water-Soluble Inorganic Ions and Potentially Toxic Metals during Wintertime in a High Population Residential Area in Beijing, China. *Processes* **2021**, *9*, 552. https://doi.org/10.3390/pr9030552.

[28]   Xiao, K.; Wang, Q.; Lin, Y.; Wang, W.; Lu, S.; Yonemochi, S. Approval Research for Carcinogen Humic-Like Substances (HULIS) Emitted from Residential Coal Combustion in High Lung Cancer Incidence Areas of China. *Processes* **2021**, *9*, 1254. https://doi.org/10.3390/pr9071254.